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"New Developments in Membrane-Based Chemical Separations"

by Kshama B. Jirage and Charles R. Martin

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Colorado State University
Department of Chemistry
Fort Collins, CO 80523-1872

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5. Kshama B. Jirage and Charles R. Martin

6. Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

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11. Abstract: Membrane based chemical separations is an emerging field of research. This is because membrane-based separations are potentially less energy intensive and more cost effective than competing separation methods. Polymeric membranes that contain a collection of monodisperse gold nanotubules with molecular dimensions were used to filter molecules based on their difference in size. Also, we will discuss how these tubules can be modified with thiols to separate molecules based on differences in their chemical properties.

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New Developments in Membrane-Based Separations

Kshama B. Jirage and Charles R. Martin (E-mail: crmartin@lamar.colostate.edu) are at the Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

Chemical separations are a major cost component of most chemical, pharmaceutical and petrochemical processes. Membrane-based separations are potentially important because they can be less energy intensive and more economical than competing separation technologies. However, if membranes are to make greater inroads into such industrial separation processes, higher flux and greater selectivity will be required.

Enantioseparations

Many drugs, pharmaceuticals and flavor compounds are racemic mixtures. However, it is often found that only one of the two enantiomers performs the required biological action. The unwanted enantiomer is, in a sense, an impurity and may cause unwanted side effects[1]. The US Food and Drug Administration (FDA) has recently declared that, if a drug is chiral, the biological effects of both the enantiomers must be studied[2]. Thus, chiral separations are becoming increasingly important.

Chiral separations are most commonly done by electrophoretic and chromatographic techiniques. There have been several attempts to use membrane-based separation methods due their advantages in terms of their cost-effectiveness and lower energy consumption. Hinze and co-workers[3] have described a new method for chiral separations in which surfactants were used to facilitate the separation of enantiomers from a racemic mixture. Chiral surfactants

have been used in several instances of chromatography and electrophoresis to achieve enantioseparations[4]. However, for the first time, the use in liquid membrane systems of bile salts and quartenary ammonium ionene salts (which are chiral) has been reported to achieve separation of enantiomeric dansyl amino acids.

Aoki et.al.[5] describe the synthesis of a novel nobornadiene polymeric membranes, with optically active pendant groups that show enantioselectivity. These membranes were used to separate the optical isomers of propronalol, a pharmaceutical product. This group has reported several polymeric membranes in the past with chiral separation properties, but the fluxes were low and the membranes were unstable[6]. The new polymer shows enhanced selectivity and flux. Enantiomeric excesses of 45% (propronalol), 66% (phenylethylalcohol) and 82% (tryptophan) were achieved with these new polymeric membranes.

A novel and simple method for optical resolution of enantiomers of tryptophan has also been recently described[7]. Polypyrrole(Ppy) membranes containing chiral anionic polymeric counterions such as poly(L-glutamic acid) (PGA) or dextran sulfonic acid (DA) were synthesized. The chiral counterions act as molecular recognition agents for the separation of enantiomers. Ogata demonstrated that Ppy membranes with achiral counter ions (Cl⁻ or polyacrylic acid) did not show any enantioselectivity but, when PGA or DA was used as the counter ion the flux of one of the enantiomers was enhanced. Also, the flux of a molecule can be enhanced by applying a potential pulse to the Ppy membrane, which may be due to the weakening of the ionic interactions in the polymer[7].

Abe and co-workers demonstrated an optical resolution method for the D and L amino acids (AAs) by using a combination of an enzyme reaction and membrane extraction[8]. They used the enzyme, α-chymotrypsin, to hydrolyse the

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enantiomers of the esters of the amino acid; this enzyme is known to selectively hydrolyse the L-AA ester in preference to the D-AA ester. The reaction mixture was placed in a hollow fiber membrane, and the unreacted ester was removed by extraction with organic solvents. A method was also developed to recycle the enzyme by preparing surfactant coated enzymes, which are insoluble in aqueous media and, so easy to recover and reuse.

An apoenzyme-based facilitated-transport membrane for enantioseparations has also been recently described[9]. With the apoenzymes immobilized within a polypyrrole-sandwich membrane, such apoenzyme-containing membranes selectively transport substrates for the apoenzyme. For example, when D-AA oxidase is immobilized in this way, the membrane selectively recognises and transports D-phenylalanine over L-phenylalanine.

Nanofiltration, permselective and metal ion separation membranes

Recently, nanofiltration (NF) membranes have attracted a great deal of attention because they have molecular weight cut off in the range 200 to 1000 Daltons, which is intermediate between conventional reverse-osmosis (RO) and ultrafiltration (UF) membranes. NF membranes are typically either positively or negatively charged and are, therefore, ion permselective[10]. At present, commercially available NF membranes are made of polymeric materials[11], which are are very stable in acidic or basic solutions. There have been attempts to fabricate inorganic NF membranes, which have the additional advantage that they can be either positively or negatively charged, depending on the pH[12], as a result, these inorganic membranes can also be ion permselective.

The fabrication of inorganic NF membranes from silica-zirconia sols has recently been described[10]. When a solution containing metal ions and the hydronium ion was used as the feed, these membranes selectively transported the

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hydronium ion in preference to the metal ions, thus concentrating the metal ions in the feed.

Ion exchangers are another class of industrially important membranes, finding uses in chlor-alkali production, fuel cells, etc[13]. Ion-exchange membranes are typically ionomers in which the ionisable groups are attached to the polymeric backbone. Cation-permselective membranes have anionic sites (e.g. sulfonate) attached and anion permselective membranes have fixed cationic groups (e.g. quartenary ammonium ions).

Metal-nanotubule membranes, with electrochemically switchable ion-transport selectivity[14], can be reversibly switched between cation-permselective and anion-permselective states. Consequently, these membranes can be viewed as universal ion exchange membranes. The metal nanotubule membranes were prepared by electroless deposition of gold within the pores of a microporous filtration membrane. A hollow gold tubule is deposited within each pore of this "template" membrane[15]. The inner diameter of these gold tubules can be controlled at will by varying the deposition time. Indeed, tubules with inside diameters of molecular dimensions (<1 nm) can be obtained[16]. The nanotubules can be charged by applying an electrical potential, in the same way that the surface of an electrode is charged, when a potential is applied to the electrode. By applying negative potentials[14], excess negative charge is placed on the gold tubule walls, and by applying positive potentials, excess positive charge is placed on the tube walls. If the tubules inner diameter is small relative to the thickness of the electrical double layer created at the charged gold tubule surfaces, these membranes transport ions of charge opposite to the applied surface charge, and reject ions of the same sign as the surface charge (Figure 1). Because the surface charge can be reversibly switched by changing the applied potential, the

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ion-permselectivity can also be reversibly switched. Cation permselectivity as high as that of the commercially available Nafion ion-exchange polymer can be obtained[14].

Novel polymeric composite films formed as multilayers of amine-terminated dendrimers and poly(maleic anhydride)-c-(methyl vinyl ether) grafted onto gold-coated silicon wafers have been recently developed[17]. These composite membranes exhibit fully reversible, pH-switchable, ion-permselectivity (Figure 2). This is possible because at low pH the $-NH_2$ groups are protonated ($-NH_3^+$), and so the membrane rejects cations. Similarly, at higher pH values the -COOH groups are deprotonated (COO^-) and the membrane rejects anions.

There have also been some new developments in the field of membranes for selective metal-ion extraction and transport. Talanova et.al.[18], Schow et.al.[19] and Wang et.al.[20], describe the synthesis of macrocyclic carriers and their use in membranes for metal ion separations. Talanova et.al. report the synthesis of a new calix[4]arene, with carboxamide side groups with tunable acidity, which has excellent extraction capabilities for lead ions over most alkali, alkaline earth and transition metal ions. Schow et.al. describe the development of a cellulose triacetate polymeric membrane with a crown ether incorporated as a carrier. They studied the properties and stability of these membranes for metal ion removal Figure 3, shows the flux of Na^+, K^+ and Rb^+ across a polymeric membrane incorporated with a crown ether. The selectivity observed by the authors is consistent with the thermodynamic stability of the crown ether with these ions as well as the trend in transport of these ions in other liquid membrane systems. Wang et.al. also reported the synthesis of new crown ethers, and they studied their solvent extraction and membrane separation properties. Sata[21] has

reviewed recent work in ion-exchange membranes with permselectivity for specific ions in electrodialysis.

Gold nanotubule molecular-filtration membranes

It has been demonstrated that gold nanotubule membranes discussed above can be used to separate small molecules (<400 Da) on the basis of molecule size[16]. For example, a gold nanotubule membrane with inner diameter of<1 nm can be used to cleanly separate pyridine from quinine. Figure 4, shows the UV absorbance spectra of the feed and the permeate solutions in a molecular-separation experiment. Such clean molecular filtrations have been accomplished for a number of small-molecule/large-molecule pairs[16].

The sulphur atom in thiols forms a strong chemical bond with some noble metals like silver and gold. This phenomenon where the adsorption is due to the formation a chemical bond is termed chemisorption. This chemistry has been studied a great detail[22] and has been used to change the chemistry of surfaces[23, 24]. Hulteen et.al.[25] showed that the chemical environment within the gold tubules can be modified by chemisorbing thiols to the inner gold tubule walls. When a hydrophobic thiol was chemisorbed in this way, the resulting membrane showed selective transport for hydrophobic molecules (e.g. toluene) over hydrophilic molecules (e.g. pyridine). Furthermore, these hydrophobic gold nanotubule membranes did not show any permeability to ionic species. By contrast, when a hydrophilic thiol was chemisorbed, the opposite selectivity pattern - selective transport of hydrophilic rather than hydrophobic molecules - was observed.

Gas separation and pervaporation

A partially-doped form of polypyrrole can show tremendous selectivity for O_2 over N_2 flux, at low partial pressures of O_2[26]. Kuwabata and co-workers have

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investigated in depth the gas-transport properties of a conducting polymer, polyaniline[27]. They observed that the permeability coefficients for all gases studied decreased with increasing doping level, and selectivity coefficients increased in general. They also studied the effects of changing the nature of the counterion, the temperature and duration of thermal processing of the film. Furthermore, the paper discusses the selecitivity for oxygen and nitrogen separation, an industrially important separation. Ulbricht and co-workers demonstrated that high performance photo-graft composite membranes for the separation of methanol and water[28]. Chen et.al describe chitosan-silk fibroin complex membranes and their application in pervaporation[29]. Yeom et.al.[30] studied polyvinylalcohol-sodium alginate composite for separation of ethanol-water mixtures. Finally, it has recently been shown that sulfonated polystyrenes can show high selectivities for methanol vs. methyl t-butyl ether transport[31].

Conclusions

Membrane-Based separations are becoming increasingly popular, offering several advantages over conventional methods of separations. The opportunities are immense, with inroads being made in new fields everyday. The major hurdles being lower fluxes and selectivities which are improved upon, will make them more viable In large-scale industrial separations.

Acknowledgements

Figure Captions

Figure 1. Schematic of switchable ion-selective gold nanotubule membrane. Applying a negative potential to the gold, allows for the passage of cations but prevents the passage of anions.

Figure 2. Schematic of pH-switchable polymer composite membrane. At low-pH the polyamine dendrimer units are protonated and prevent the passage of cations and at high pH, the film has negatively charged groups which prevent the passage of anions.

Figure 3. Plot of Na^+ (diamonds), K^+ (hollow squares) and Rb^+ (solid squares) transported simultaneously across a polymer inclusion membrane with dicyclohexano-18-crown-6 ether.

Figure 4. UV absorbance spectra of a) 0.5 mM pyridine and 0.5 mM quinine b) A mixture of pyridine and quinine (0.25 mM each) c) permeate after transport through gold nanotubule membrane after 72 hours.

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